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METHOD FOR IMPROVING LIGHT RESISTANCE OF DYE

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[Attached amendments have been incorporated into text of translation.]

Claims

1. A method for improving the light resistance of a dye, characterized by the fact that an inclusion compound of dye and cyclodextrin is formed.

2. A method for improving light resistance as in Claim 1, wherein the cyclodextrin is β-cyclodextrin.

3. A method for improving light resistance as in Claim 1, wherein the cyclodextrin is 2,4,5-tris-O-methyl-γ-cyclodextrin.

4. A method for improving light resistance as in any of Claims 1-3, wherein the dye is methylene blue.

Detailed explanation of the invention

Industrial application field

This invention pertains to the light resistance of a dye to be used in a coloring agent.

Prior art

As a conventional method for preventing the optical discoloration of a dye, in general, ultraviolet absorbents and antioxidants were used. Figure 2 shows the cross section of textile printed substance in which a conventional method for preventing optical discoloration is carried out by using the antioxidant described in Vol. 88, No. 122 (issued in 1985) of "Chemistry and Industry"). (1) is the dye. (4) is the supporting body. (5) is the antioxidant. (6) is the coloring layer. Next, the function is explained. A dye (abbreviated as D in the equation) is decomposed through the path of: excited singlet dye (abbreviated as ^1D in the equation) → excited triplet (^3D in the equation) → decomposed substance (abbreviated as product in the equation). In other words, this can be expressed by the following equations (1)-(6).

$$D \xrightarrow{h\nu} {}^1D \qquad (1)$$

$${}^1D \xrightarrow{k_0} D \qquad (2)$$

$${}^1D \xrightarrow{k_f} D + h\nu \qquad (3)$$

$${}^1D \xrightarrow{k_{ST}} {}^3D \qquad (4)$$

$${}^3D \xrightarrow{k_0'} D \qquad (5)$$

$${}^3D + O_2 \xrightarrow{k_p} \text{product} \qquad (6)$$

In the equations, k_0 is the rate constant of a radiationless transition of the singlet dye to the ground state, k_F is the rate constant of the transition of the singlet dye to the ground state, and k_p is the rate constant for the reaction between triplet dye and oxygen. As the above-mentioned method for preventing the discoloration, a conventional antioxidant (abbreviated as AH in the equation) was used, and the discoloration was prevented as shown in the following equations (7) and (8):

$$^3D + O_2 \xrightarrow{k_1} DOO \qquad (7)$$

$$DOO + 4AH \xrightarrow{k_t} D + 4A\cdot + 2H_2O \qquad (8)$$

where k_1 is the rate constant for the coupling of the triplet dye and oxygen, and k_t is the rate constant for the decomposition of the dye peroxide.

Problem to be solved by the invention

When the optical discoloration was prevented by the above-mentioned conventional antioxidant, on the contrary, discoloration was also promoted by reductive discoloration due to the antioxidant expressed by the following equation:

$$^3D + AH \rightarrow DH + A\cdot \qquad (9)$$

The present invention solves that problem, and its purpose is to improve the light resistance of a dye.

Means to solve the problem

Means to solve the problem

The method of the present invention for improving the light resistance of a dye forms an inclusion compound from dye and cyclodextrin.

Function

The cyclodextrin (abbreviated as CD in the equation) of this invention forms a dye and an inclusion compound and quenches the singlet dye as expressed in the following equations (10) and (11). In other words, the [reaction of] equation (10) is generated, or the value of k_o of equation (2) is increased:

$$^{1}D + CD \xrightarrow{kq} D + {}^{1}CD \tag{10}$$

$$^{1}CD \xrightarrow{k_o''} CD \tag{11}$$

where k_q is the rate constant for energy transfer from the singlet dye to cyclodextrin, k_o'' is the rate constant of the radiationless transition of singlet cyclodextrin, and ^{1}CD is excited singlet CD.

At this moment, the discoloration rate of the dye is expressed by the following equations (12)-(17).

$$\frac{d[D]}{dt} = -\phi I[D] + k_o[^{1}D] + k_f[^{1}D] + k_o'[^{3}D] + kq[^{1}D][CD] \tag{12}$$

$$\frac{d[^{1}D]}{dt} = \phi I[D] - k_o[^{1}D] - k_f[^{1}D] - k_{ST}[^{1}D] - kq[^{1}D][CD] \tag{13}$$

$$\frac{d[^{3}D]}{dt} = k_{ST}[^{1}D] - k_o'[^{3}D] - k_p[^{3}D][O_2] \tag{14}$$

In the steady state, $d[{}^1D]/dt = 0$ and $d[{}^3D]/dt = 0$. In other words,

$$[{}^1D] = \frac{\phi I\,[D]}{k_o + k_p + k_{ST} + k_q[CD]} \tag{15}$$

$$[{}^3D] = \frac{k_{ST}[{}^1D]}{k_o' + k_p\,[O_2]} \tag{16}$$

$$= \frac{k_{ST}}{k_o' + k_p[O_2]} \cdot \frac{\phi I\,[D]}{k_o + k_p + k_{ST} + k_q[CO]}$$

Equation (17) is obtained by inserting the equations (15) and (16) into the equation (12).

$$\frac{d[D]}{dt} = \frac{-k_p k_{ST}[O_2]\,\phi I}{k_o + k_p + k_{ST} + k_q[CD]}\,[D] \tag{17}$$

From equation (17), it is understood that if k_o, k_p, and $k_q \cdot [CD]$ are increased, the discoloration rate is reduced; for this reason, cyclodextrin is added.

Application example

Figure 1 is a constitutional diagram of an inclusion compound of dye and cyclodextrin of an application example of the present invention. (1) is a dye. (2) is a cyclodextrin. (3) is an inclusion compound.

As the cyclodextrin of this invention, for example, α-cyclodextrin, β-cyclodextrin, γ-cyclodextrin, 2,4,5-tris-O-methyl-γ-cyclodextrin and a polymer containing water-soluble cyclodextrin (described in Japanese Kokai Patent Application No. Sho 58[1983]-167613), etc., can be used.

As the dye of this invention, for example, methylene blue, Malachite Green, Basic Orange 21, Basic Red 13, Basic Blue 25, Basic Brown 1, etc., are used.

As a method for forming the inclusion compound of the cyclodextrin and the dye of this invention, the cyclodextrin and dye are dissolved in an appropriate solvent such as dimethyl sulfoxide and then dried.

Next, this invention is explained in detail by the application examples.

Application Example 1

Methylene blue at 0.01 part by weight and β-cyclodextrin at 1 part by weight are dissolved in dimethyl sulfoxide at 100 parts by weight, and a piece of filter paper was immersed in the solution, pulled up and dried. After the filter paper was irradiated by the light of a super-high-pressure mercury lamp for 2, 5, 7 and 10 min, producing the characteristic diagram of the change in the optical density (OD) shown in Figure 3(a). In the figure, the ordinate represents OD (optical density), and the abscissa represents the irradiation time (min).

Comparative example

Only methylene blue at 0.01 part by weight is dissolved in dimethyl sulfoxide at 100 parts by weight, and a piece of filter paper is immersed into the solution, pulled up and dried. After light from a super-high-pressure mercury lamp is irradiated on the filter paper for 2, 5, 7 and 10 min, the optical density is as shown in Figure 3(b).

Comparing the above-mentioned Figure 3(a) with (b), it is understood that the light resistance is improved in (a).

Effect of the invention

As explained above, this invention can improve the light resistance of a dye by forming an inclusion compound of the dye with cyclodextrin.

Brief explanation of the figures

Figure 1 is a constitutional diagram of an inclusion compound of an application example of the present invention. Figure 2 is a cross section of a conventional textile printed substance. Figure 3 is a characteristic diagram that shows the comparison of the light resistance of the dye of an application example of the present invention and that of a conventional dye.

In the figures, (1) is a dye. (2) is a cyclodextrin. (3) is an inclusion compound.

Also, identical symbols in the figures represent identical or corresponding parts.

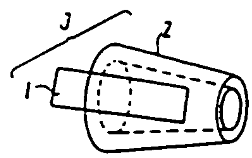

Figure 1

Key: 1 Dye
2 Cyclodextrin
3 Inclusion compound

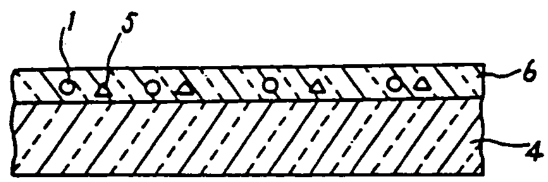

Figure 2

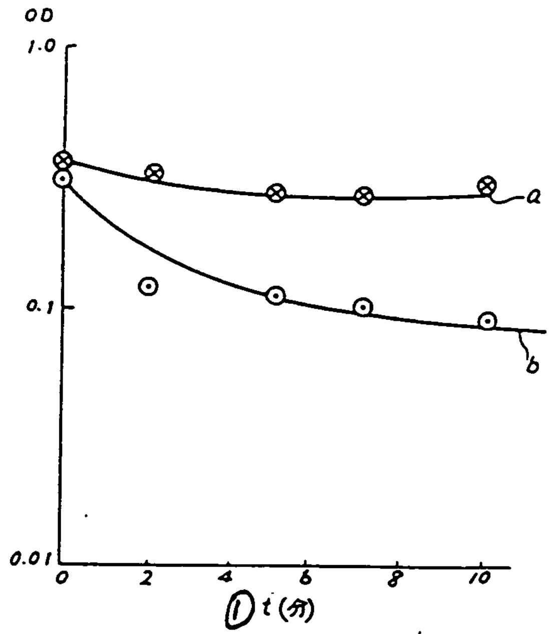

Figure 3

Key: 1 t (min)